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(19)

(54) DETERGENT COMPOSITIONS AND COMPONENTS THEREOF

(71) We, COLGATE-PALMOLIVE COMPANY, a Corporation organised under the laws of the State of Delaware, United States of America, of 300 Park Avenue, New York, New York 10022, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to detergent compositions and components thereof. In particular, the invention pertains to the manufacture of free flowing detergent builder beads (hereinafter referred to also as base builder beads) capable of carrying relatively large amounts of various liquid or liquefiable detergents and other liquid or liquefied organic materials suitable for incorporation into detergent compositions. The invention provides a method for producing spray dried base builder beads that can be oversprayed with synthetic detergents such as nonionics, anionics and cationics or combinations thereof to produce particulate detergent compositions of improved detergency and solubility and that contain relatively large amounts of the synthetic detergent component while retaining free flowing properties. As used herein the terms "overspray" and "post spray" are synonymous and include any suitable means for applying a liquid or liquefiable substance to the base builder beads, such as spraying the liquid through a nozzle in the form of fine droplets. The invention is particularly useful in providing a particulate free flowing detergent composition having a high content of nonionic synthetic organic detergent.

Typically, nonionic synthetic detergents having the desired detergency properties for incorporation into commercial particulate detergent products, such as laundry powders, are thick, viscous, sticky liquids or semi-solid or waxy materials. The presence of these materials in a detergent slurry (crutcher mix) prior to spray drying in amounts greater than about 3 percent by weight is impracticable since the nonionic synthetic detergent will "plume" during spray drying and a significant portion can be lost through the gaseous exhaust of the spray drying tower.

The art has recognized the application of nonionic synthetic detergents of this type to various particulate carrier bases to produce relatively free flowing particulate products that can be used for household laundry. Representative patents containing teachings and disclosures of methods for producing particulate free flowing laundry detergents by post spraying a nonionic synthetic organic detergent onto a spray dried particulate product containing detergent builders include, among others: U.S. Patents 3,538,004, 3,849,327, 3,888,098 and 3,888,781, and British Patent 918,499. The prior art is typified by post spraying from about 1 to a maximum of 10 percent by weight of a nonionic synthetic detergent onto a spray dried bead that contains a substantial proportion of a surface active agent such as an anionic detergent, filler materials, and detergent builders.

Further, certain desirable ingredients for detergent compositions, such as cationic surface active agents that provide fabric softening properties, and optical brighteners, bluing agents and enzymatic materials, cannot be spray dried because of thermal decomposition. Such materials can be incorporated into particulate detergent composition by post spraying them onto spray dried base builder beads in accordance with this invention, either alone or in addition to a nonionic detergent or other suitable ingredients.

According to one aspect of the invention a method for producing a free flowing particulate detergent composition comprises hydrating a first quantity of anhydrous phosphate builder salt in the presence of a second quantity of alkali metal silicate to form a hydrated aqueous slurry, adding a third quantity of anhydrous phosphate builder salt to the hydrated slurry to form a crutcher mix, the weight ratio of the first quantity to the second quantity being in the range from 1.5:1 to 5:1 and the weight ratio of the first quantity of the third quantity being in the range from 0.3:1 to 0.7:1, spray drying the crutcher mix to form builder beads having a porous outer surface and a skeletal internal structure, and applying to the beads a liquid or liquefiable material comprising an organic detergent.

The base builder beads are suitable for carrying relatively large amounts, e.g. from 2 to 40 percent by weight, preferably from 12 to 40 percent, of various materials suitable for incorporation into detergent compositions, such as anionic, nonionic, and cationic surface active agents, optical brighteners, bluing agents, soil release agents, antiredeposition agents, and mixtures thereof. The post added detergent ingredients are applied in liquid form onto the base builder beads by any suitable means, preferably by spraying in the form of fine droplets from a spray nozzle while the beads are being agitated. The invention contemplates the post spraying of any liquid or liquefiable organic material suitable for incorporation into a laundry detergent formulation, onto the spray dried base builder beads comprising inorganic detergent builders.

Such beads and a method of manufacturing them are the subject of our divisional application, British patent application No. 79298/36 (Serial No. 1579262).

The base builder beads of the invention are normally spherical or irregularly shaped beads comprising by weight from 45 to 90 percent phosphate builder salt, from 5 to 15 percent alkali metal silicate solids and from 5 to 15 percent water. From 30 to 60 percent by weight of the alkali metal phosphate component is hydrated in the presence of the alkali metal silicate component and the remainder is in anhydrous form. The beads have a porous, sponge-like outer surface and a skeletal internal structure, in contrast to the hollow beads typical of spray dried powders.

The post sprayed ingredients are wholly or predominantly disposed within the beads with only minimal amounts, if any, present on the outer surface of the beads. The resulting product is free flowing and without a significant tendency of the post spraying beads to stick together or agglomerate. Desirably less than 10 percent by weight of the over-sprayed material is present on the outer surface of the final beads.

The free flowing ability of a particulate substance can be measured in relation to the flowability of clean dry sand under predetermined conditions, such as inclination with the horizontal plane, the sand being assigned a flowability value of 100. Typical spray dried detergent powders as presently available on the market having a flowability of about 60 in relation to sand, i.e. 60 percent of the flowability of sand under the same conditions. Surprisingly, particulate compositions embodying the invention may have a flowability of at least 75, and in some cases 90 or more.

The base builder beads according to the invention can usually be further characterised as follows:

Particle size distribution: at least about 90% by weight passing through a 20 mesh screen (U.S. series) and being retained on a 200 mesh screen (U.S. series) Specific gravity: 0.5—0.7. Flowability: 70—100.

The base builder beads of the invention can be produced as follows:

A first quantity of a hydratable alkali metal phosphate builder salt is hydrated in the presence of a second quantity of an alkali metal silicate: the weight ratio on an anhydrous basis of the first quantity to the second quantity generally being in the range from 1.5:1 to 5:1. The hydrated phosphate and silicate are mixed in an aqueous medium, at a temperature in the range of 140°F to 170°F, with a third quantity of anhydrous alkali metal phosphate builder salt to form a slurry or crutcher mix, the weight ratio of the first quantity to the third quantity generally being in the range from 0.3:1 to 0.7:1. Various other detergent ingredients, e.g. in an amount up to 10% by weight builders such as carbonates, citrates, silicates and organic builders, and surface active agents can be added to the crutcher mix after the hydration step. It is preferred that organic surface active agents in the crutcher mix be limited to less than 2 percent by weight of the solids present and most preferably that the crutcher mix be free from organic surface active agents. The

crutcher mix is agitated and maintained at a temperature in the range from 170°F to 200°F to prevent any significant hydration of the third quantity of anhydrous phosphate builder salt. Water is usually present in the slurry in an amount such that the crutcher mix contains from 40 to 55 percent by weight of solids. Adjuvents such as brighteners, bluing, or other minor ingredients may be present in the crutcher mix if necessary or desirable, or may be added to the spray dried beads.

The crutcher mix is then pumped to a spray tower where it is spray dried in the conventional manner. The spray drying may be performed in a countercurrent or co-current spray drying tower using an air inlet temperature in the range from 500 to 700°F and a spray pressure in the range from 200 psig (lbs./sq. in. gauge) to about 1000 psig. The spray dried product comprises numerous base builder beads having the structure already described, in contrast to the hollow structure that typically results from spray drying a detergent crutcher mix.

According to another aspect of the invention there is provided a free flowing particulate detergent composition suitable for domestic or commercial laundering of textile materials. The composition may have a nonionic synthetic organic detergent content in the range from 10 to 40 percent by weight, preferably from 12 to 30 percent by weight, although lower percentages of nonionic detergent may sometimes be used, e.g. 3 to 5%. Preferably the composition is devoid of filler materials such as alkali metal sulphates that are commonly used in spray drying detergent powders to obtain high spray drying rates and which are present in the resulting products. The detergent compositions of the invention can be used as such as complete laundry detergents, or various additional ingredients can be added thereto such as perfumes; colouring agents; bleaches, e.g. 15 to 50% by weight of an alkali metal per-salt bleach, such as sodium perborate, sodium percarbonate, potassium percarbonate, potassium perborate and mixtures thereof; brighteners, e.g. 0.01 to 2% by weight of stilbene and triazolyl brighteners; fabric softeners, e.g. 0.1 to 5% by weight of quaternary ammonium halides, such as di-higher alkyl di-lower alkyl ammonium chloride; and 0.2 to 4% by weight of enzymes such as proteolytic enzymes of the types sold by Novo Industries under the name "Alcalase" (Registered Trade Mark) and "Esperase", (Registered Trade Mark), or amylolytic enzymes or mixtures thereof.

A method for producing the particulate detergent compositions may include the steps of first providing numerous base builder beads having the above mentioned physical characteristics. The nonionic synthetic detergent is then applied on to the spray dried base builder beads while they are being agitated, preferably in an amount in the range from 10 to 40 percent by weight of the final composition. The nonionic synthetic detergent impregnates the pores or openings in the surface of the beads and passes into the skeletal internal structure; an insignificant amount, if any, of the nonionic detergent remains on the bead surface. The presence of at most a minimal amount of nonionic detergent on the outer surface of the beads is evidenced by the substantially similar flowability rates obtained for the beads before and after they have been sprayed with the nonionic detergent. A similar method may be used to apply other post added ingredients to the spray dried base builder beads.

The accompanying illustrations are photomicrographs of a spray dried base builder bead according to the invention prior to being post sprayed.

Figure 1 shows a major portion of the bead, the magnification being ascertainable by reference to the line below the photomicrograph which represents a length of 1/200 inch. If the illustration were enlarged to have a side of 20 cm the magnification would be 200×.

Figure 2 shows a portion of the bead of Figure 1 at a magnification ten times that of Figure 1.

As shown in the illustrations the base builder beads are solid particles of irregular configuration that have a sponge-like, porous outer surface and a skeletal internal structure. In contrast, conventional spray dried detergent beads such as those currently available on the consumer market typically comprise spherical beads with a substantially non-porous outer surface and a hollow core.

The base builder beads preferably comprise, by weight, from 45 to 80 percent phosphate builder salt, preferably from 50 to 70 percent; from 5 to 15 percent alkali metal silicate solids, and 5 to 15 percent water. However, although the product will not usually be as free flowing, when lesser amounts of phosphate are employed, such as 20 to 25% (usually when nonionic detergent and water contents are low, too) a useful product can be made.

According to a preferred aspect of the invention, a substantial portion of the

builder salt component of the base beads is the product of hydrating to a maximum degree, typically to the hexahydrate form, from 30 to 60 percent of the phosphate builder salt in the presence of the alkali metal silicate. The weight ratio on an anhydrous basis of the hydrated phosphate builder salt to the alkali metal silicate in both the crutcher mix and the base beads is in the range from 1.5:1 to 5:1 preferably 2:1 to 4:1, and the weight ratio on an anhydrous basis of the hydrated phosphate builder salt to the anhydrous builder salt in the crutcher mix and the base beads is in the range from 0.3:1 to 0.7:1, preferably 0.4:1 to 0.6:1.

In its presently preferred form, the crutcher mix of the invention contains only inorganic detergent builders and water and is free from organic surface active agents. Most preferably the crutcher mix is also free from filler materials such as sodium sulphate.

The phosphate builder salt component of the base builder beads is chosen from phosphate salts having detergent building properties. Examples of phosphate builder salts having detergent building properties are the alkali metal tripolyphosphates and pyrophosphates, of which the sodium and potassium compounds are most commonly used. These phosphates are well known in the detergent art as builders and can either be used alone or as mixtures of different phosphates. More specific examples of phosphate builder salts are: sodium tripolyphosphate; tetrasodium pyrophosphate; dibasic sodium phosphate; tribasic sodium phosphate; monobasic sodium phosphate; dibasic sodium pyrophosphate; and monobasic sodium pyrophosphate. The corresponding potassium salts are also examples, as are mixtures of the potassium and sodium salts.

The alkali metal silicate component of the crutcher mix may be supplied in the form of an aqueous solution, preferably containing from 40 to 60 percent by weight, typically about 50 percent by weight, of silicate solids. Preferably the silicate component is sodium silicate with an $Na_2O:SiO_2$ ratio in the range from 1:1.6 to 1:3.4, preferably from 1:2 to 1:3, and most preferably about 1:2.4.

The overspray ingredients or components can include any liquid material or material capable of being liquified that is suitable or desirable for incorporation into a detergent composition. Suitable materials for overspraying onto the spray dried builder beads in amounts in the range from 2 to 40 percent by weight include, but are not limited to, surface active agents, anti-redeposition agents, optical brighteners, bluing agents and enzymes.

Suitable surface active agents include anionic and nonionic detergents, and cationic materials. Typical anionic materials include soap, organic sulphonates such as linear alkyl sulphonates, linear alkyl benzene sulphonates, and linear tridecyl benzene sulphonate. Representative cationic materials are those having fabric softening or antibacterial properties such as quaternary ammonium compounds. These last mentioned cationic materials are particularly suitable for post addition since they might thermally decompose if spray dried as part of a crutcher mix. Examples of quaternary compounds having desirable fabric softening properties are distearyl dimethyl ammonium chloride (available from Ashland Chemical Company, U.S.A. as "Arosurf TALOO") and 2 - heptadecyl - 1 - methyl - 1 - [(2 - stearoylamido) ethyl] imidazolinium methyl sulphate (also available from Ashland Chemical Company as "Varisoft 475").

The nonionic surface active agent component can be a liquid of semi-solid (at room temperature) polyethoxylated organic detergent. Preferably, these include but are not limited to ethoxylated aliphatic alcohols having straight or branched chains of from 8 to 22 carbon atoms and from 5 to 30 ethylene oxide units per molecule. A particularly suitable class of nonionic organic detergents of this type are available from the Shell Chemical Company, U.S.A. as the "Neodol" range. "Neodol 25-7" (12—15 carbon atom alcohol chain; average of 7 ethylene oxide units) and "Neodol 45-11" (14—15 carbon atom chain; average of 11 ethylene oxide units) are particularly preferred.

Another suitable class of ethoxylated aliphatic alcohol nonionic synthetic detergents are available as the "Alfonic" (Registered Trade Mark) range from Continental Oil Company U.S.A., particularly "Alfonic 1618-65", which is a mixture of ethoxylated 16 to 18 carbon atom primary alcohols containing 65 mole percent ethylene oxide.

Further examples of nonionic synthetic organic detergents include:

1) Those available under the trademark "Pluronic". These compounds are made by condensing ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol. The hydrophobic portion of the molecule, which exhibits water insolubility has a molecular weight of from

about 1500 to about 1800. The addition of polyoxyethylene radicals to this hydrophobic portion tends to increase the water solubility of the molecule as a whole, and the liquid character of the product is retained up to the point where the polyoxyethylene content is about 50 percent of the total weight of the condensation product.

2) The polyethylene oxide condensates of alkyl phenols, e.g. the condensation products of alkyl phenols having an alkyl group containing from 6 to 12 carbon atoms in either a straight chain or branched chain configuration, with ethylene oxide, the ethylene oxide being present in amounts corresponding to 5 to 25 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds may be derived from polymerized propylene, diisobutylene, octene or nonene, for example.

Other surface active agents that may be suitable are described in the texts, "Surface Active Agents and Detergents", Vol. II, by Schwarz, Perry and Berch, published in 1958 by Interscience Publishers, Inc., U.S.A. and Detergent and Emulsifiers, 1969 Annual by John W. McCutcheon, U.S.A.

A particularly preferred detergent composition embodying the invention comprises from 12 to 30 percent by weight of nonionic synthetic organic detergent, most preferably of the polyethoxylated aliphatic alcohol type, oversprayed onto spray dried base builder beads produced according to the method of the invention.

The following Examples are illustrative of the invention (all percentages are by weight unles otherwise specified).

EXAMPLE I

An aqueous slurry of the following ingredients is prepared.

Ingredient	Amount, Percent (based on total crutcher mix)
Sodium tripolyphosphate powder (anhydrous)	14.5
Sodium silicate solids (Na_2O/SiO_2=2.4)	7.6
Water	28.6

The slurry is brought to a temperature of about 140°F and mixed well to form the hexahydrate phosphate salt and is subsequently heated to 190°F and maintained between 190°F and 200°F to prevent hydration of the next to be added phosphate ingredients.

The following ingredients are then added to the aqueous slurry at 190° to 200°F to form a crutcher mix.

Ingredient	Amount, Percent (based on total crutcher mix)
Sodium tripolyphosphate powder (anhydrous)	28.3
Water	21.0

The crutcher mix contains from about 45 to about 50 percent solids.

The crutcher mix is supplied to a countercurrent 8 feet high spray drying tower and is sprayed at a manifold temperature of 180°F and a pressure of 600—900 psig using a "Whirljet 15-1" or "Fulljet 3007" spray nozzle.

An air inlet temperature (T_1) of about 600°F is used in the spray tower.

The spray dried base beads produced have the following properties and are similar in internal structure and outer surface characteristics to the bead shown in the accompanying photomicrographs.

Base Bead Properties		
Moisture	10%	
Tripolyphosphate (Sodium salt)	77%	
Silicate solids	13%	
Cup Weight	130 g	(Apparent specific
Flow	86	gravity=0.55 or bulk
Tack	0	density=0.55 g/ml)

Size Analysis:	
On U.S. 20 Mesh	1%
On U.S. 40 Mesh	19%
On U.S. 60 Mesh	50%
On U.S. 80 Mesh	20%
On U.S. 100 Mesh	6%
On U.S. 200 Mesh	3%
Through U.S. 200 Mesh	1%
	100%

The base beads are then introduced into a batch rotary drum blender and post sprayed with "Neodol 25-7" at 120°F and minor ingredients such as colouring agents, perfume and brighteners, to produce a final product as follows:

Base Bead (above)	78 %
"Neodol 25-7" (at 129°F)	19.7%
Minors (Colour, Perfume, Brightener)	2.3%
	100.0%

The "Neodol" is sprayed first, followed by the minors.

Any suitable batch type blender that has provision for spraying liquids, in the form of fine droplets or as a mist, such as a Patterson Kelly twin shell blender, can be used. The post addition spraying operation can also be performed on a continuous basis using suitable mixing apparatus such as the Patterson-Kelly Zig-Zag blender.

The resulting granular detergent composition has the following properties:

Finished Product Properties		
Cup Weight	160 g.	(apparent specific
Flow	79	gravity=0.68)
Tack	0	
Size Analysis		
On U.S. 20 Mesh	1%	
On U.S. 40 Mesh	20%	
On U.S. 60 Mesh	52%	
On U.S. 80 Mesh	20%	
On U.S. 100 Mesh	5%	
On U.S. 200 Mesh	2%	
Through U.S. 200 Mesh	0%	
	100%	

The finished product can be packed on conventional equipment used for packaging particulate products. Alternatively, it may be dry mixed with potassium percarbonate (or sodium percarbonate) or sodium perborate to produce products of 15 to 50% bleach content, e.g. 21.5% of potassium or sodium percarbonate and 30% of sodium perborate. Also, powdered enzyme may be post-added to make an enzymatic detergent composition (which may also contain bleach) of 0.2 to 4% enzyme preparation, e.g. 0.7% of "Alcalase" or "Esperase". Other minor constituents, such as foam control agents and stabilizers, especially bleach stabilizers, may also be post-added.

EXAMPLE 2

An aqueous slurry of the following ingredients is prepared.

Ingredients (In order of addition)	Amount, Percent (based on total crutcher mix)
Hot water (140°F)	25.0
Sodium silicate solids (Na_2O/SiO_2=2.4)	3.5
Sodium tripolyphosphate powder (anhydrous)	13.0

The aqueous slurry is mixed well in a steam jacketed vessel to hydrate the phosphate ingredient and then heated to 200°F with steam.

The following ingredients are then added to the aqueous slurry to form a crutcher mix. The temperature is maintained higher than 180°F to prevent hydration of subsequently added anhydrous phosphate builder salt.

Ingredients (In order of addition)	Amount Percent (based on total crutcher mix)
Sodium tripolyphosphate (anhydrous)	13.0
Water	25.0
Sodium tripolyphosphate (anhydrous)	13.0
Sodium carbonate	7.5

The crutcher mix is supplied to a countercurrent spray drying tower at a temperature of about 170°F and sprayed at a pressure of 800 psig. The tower conditions include a T_1 (inlet) air temperature of 650°F and a T_2 (outlet) air temperature of about 235°F.

The spray dried builder beads have a particle size distribution such that 90 percent pass through a 20 mesh screen (U.S. series) and 90 percent are retained on a 200 mesh screen (U.S. series).

The spray dried beads are oversprayed according to the technique used in Example 1 as follows:

Overspray Formula	Amount Percent
Spray dried beads	78.0
"Neodol 25-7"	19.5
Minor ingredients (optical brighteners and perfume)	2.5
	100.0

The final product has a cup weight of 180 grams; a flow of 75 percent and a water content of 5 percent.

EXAMPLE 3

The procedure of Example 2 are followed with a crutcher mix (about 50 percent solids) of the following composition:

Ingredient	Amount Percent
Sodium tripolyphosphate (hexahydrate)	13.0
Sodium tripolyphosphate (anhydrous)	26.0
Water	47.0
Organic Builder "M" (Monsanto Chemical Co.)	7.5
Sodium silicate (solids)	6.5
	100.0

The spray dried builder beads are oversprayed as follows using the technique of Example 1.

Ingredient	Amount Percent
Spray dried builder beads	85.0
Nonionic ("Neodol 45-11")	12.0
Minor Ingredients	3.0
	100.0

The resulting particulate detergent composition is free flowing, non-tacky and suitable for the home or commercial laundering of clothing.

EXAMPLE 4

Example 1 is repeated using "Alfonic 1618-65" nonionic detergent in an

amount to provide a final particulate detergent composition having a 30 percent nonionic content.

EXAMPLE 5

Crutcher mixes having the following compositions are prepared according to the procedures of Example 1.

Ingredient	Amount Percent I	II	III	IV
Sodium tripolyphosphate (hexahydrate)	10	12	18	20
Sodium silicate solids (Na_2O/SiO_2=2.4)	3	8	6	4
Sodium tripolyphosphate (anhydrous)	30	30	26	28
Water	57	50	50	48

Crutcher mixes I, II, III and IV are spray dried according to the procedures outlined in Example I. The spray dried beads are oversprayed as follows:

Ingredients	Amount Percent I	II	III	IV
Spray dried beads	74.5	80.5	59	83
Minor ingredients	0.5	1.5	1	2
"Neodol 45-11"	—	18.0	—	—
"Neodol 25-7"	25.0	—	40	—
"Alfonic 1618-65"	—	—	—	15

The resulting particulate detergent compositions from runs I, II, III and IV are free flowing and are very soluble in wash water.

EXAMPLE 6

Spray dried base builder beads produced from the crutcher mixes I—IV of Example 5 are oversprayed as follows:

Ingredient	Amount (Percent) Crutcher Mix I	II	III	IV
Spray dried base builder beads	94	79.9	73.5	79.4
"Neodol 25-7"	—	15	20	12
Linear tridecyl benzene sulphonate	—	3	—	5
"Arosurf TALOO" (sprayed at 180—210°F)	6	—	4	2
Bluing agent	—	0.1	—	0.1
Optical brightener	—	2	1.5	1
Enzymatic compound (dispersed in a vehicle)	—	—	1	0.5

The formulations II, III, and IV are suitable for use as laundry detergents. The formulation I is a fabric softener that can be used in a washing machine.

The various post spray drying ingredients of Example 6 and those of the other Examples can be applied to the base beads either separately or in any suitable combination.

EXAMPLE 7

The procedure of Example 1 is followed to produce spray dried base beads having the following composition:

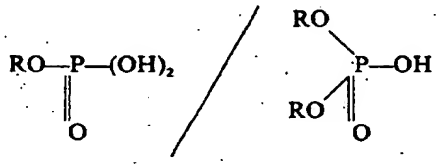
Ingredient	% by Weight
Sodium tripolyphosphate	86.031
Sodium silicate (Na_2O/SiO_2=2)	5.111
Stilbene 4 high conc.	0.852
Moisture	8.007
	100.000

The stilbene brightener is added to the crutcher mix after the initial phosphate hydration step. The crutcher mix can have a solids content from 40 to 50 percent.

The base beads are introduced into a batch rotary drum blender and the following ingredients are post-added to the base beads:

Ingredient	% in Finished Product
Nonionic detergent (7 units of ethylene oxide)	17.0
"PAE"*	1.5
Sodium percarbonate	21.5
"Sydex 808"**	0.3
"Alcalase"	0.7
Perfume	0.3

*PAE: Phosphoric acid ester from Knapsack/Hoechst named "LPKn 158". This is a C_{16}—C_{18} 2 ethylene oxide mono/diester, acid form:



functioning as an antifoam agent and also contributing to detergency.

**"Sydex 808". 92/8 magnesium silicate/diethylenetriamine pentaacetic acid (DTPA) mixture functioning as a perborate/percarbonate stabilizer.

The nonionic detergent and PAE can be melted and sprayed together onto the base beads.

In place of the sodium percarbonate bleach, sodium perborate in a slightly greater amount can be used, e.g. 30% perborate.

The final formulation has the following composition:

Ingredient	%
Sodium tripolyphosphate	50.5
Sodium silicate	3.0
Stilbene 4 high conc.	0.5
Moisture	4.7
Nonionic detergent	17.0
"PAE"	1.5
Sodium percarbonate	21.5
"Sydex 808"	0.3
"Alcalase"	0.7
Perfume	0.3
	100.0

The invention allows the production of free-flowing detergent beads by a method which does not produce pollution (fuming or pluming) and which is economically feasible, with high throughputs, utilizing conventional plant equipment. In addition to being free-flowing, the product is non-tacky and has improved water solubility relative to prior art detergent powders. Lengthy aging periods are not necessary for the spray dried detergent intermediate beads before they can be treated with the overspray ingredients, and such aging periods are not needed before filling into containers.

WHAT WE CLAIM IS:—

1. A method for producing a free flowing particulate detergent composition, comprising hydrating a first quantity of anhydrous phosphate builder salt in the presence of a second quantity of alkali metal silicate to form a hydrated aqueous slurry, adding a third quantity of anhydrous phosphate builder salt to the hydrated slurry to form a crutcher mix, the weight ratio of the first quantity to the second quantity being in the range from 1.5:1 to 5:1 and the weight ratio of the first quantity to the third quantity being in the range from 0.3:1 to 0.7:1, spray drying the crutcher mix to form builder beads having a porous outer surface and a skeletal internal structure, and applying to the beads a liquid or liquefiable material comprising an organic detergent.

2. A method according to Claim 1 including adding water to the hydrated slurry.

3. A method according to Claim 1 or Claim 2 wherein the hydrating step is performed at a temperature suitable for hydrating the first quantity of phosphate builder salt and the hydrated aqueous slurry is raised to a temperature at which hydration of the third quantity of phosphate builder salt is inhibited.

4. A method according to Claim 3 wherein the temperature to which the hydrated aqueous slurry is raised is in the range from 170°F to 200°F.

5. A method according to any of the preceding Claims wherein the crutcher mix contains from 40 to 55 percent by weight of solids, the weight ratio of the first quantity to the third quantity is about 0.5:1 and the spray drying takes place in a countercurrent spray tower at a spray pressure in the range from 200 psig to 1000 psig and an inlet air temperature in the range from 500°F to 700°F.

6. A method according to any of the preceding Claims which includes the addition to the crutcher mix of up to 10 percent by weight, based on the weight of solids, in the crutcher mix, of builder salts chosen from carbonates, citrates and silicates having detergent building properties, and mixtures thereof.

7. A method according to any of the preceding Claims in which the beads, prior to the application of the said material, are substantially free from organic surface active agents.

8. A method as claimed in any of the preceding Claims in which the material applied to the beads comprises a nonionic detergent.

9. A method according to Claim 8 wherein the builder beads comprises from 45 to 80 percent by weight of phosphate builder salt; from 5 to 15 percent by weight of alkali metal silicate solids and from 5 to 15 percent by weight of water, and the material comprising a nonionic detergent is applied in an amount of from 12 to 30 percent by weight of the detergent composition.

10. A method according to any of the preceding Claims wherein the said material is applied to the beads while the beads are being agitated.

11. A method according to any of the preceding Claims wherein the said material includes a bleach.

12. A method according to any of the preceding Claims wherein the said material includes an enzyme.

13. A method of producing a free flowing particulate detergent composition including from 2 to 40 percent by weight of a liquid or liquefiable material comprising an organic detergent, which method comprises:

a) hydrating a first quantity of anhydrous sodium tripolyphosphate builder salt in the presence of a second quantity of sodium silicate to form a hydrated slurry, the hydration being performed in an aqueous medium and at a temperature in the range from 140°F to 170°F, and the weight ratio of the first quantity to the second quantity being in the range from 1.5:1 to 5:1;

b) raising the temperature of the hydrated slurry into the range from 170°F to 200°F;

c) adding a third quantity of anhydrous sodium tripolyphosphate to the heated hydrated slurry to form a crutcher mix;

d) supplying the crutcher mix to a spray drying tower, the hydrated slurry and the crutcher mix being maintained at temperatures of at least 170°F through the steps (c) and (d);

e) spraying the crutcher mix in the spray drying tower to produce spray dried builder beads having a porous outer surface and a skeletal internal structure; and

f) applying the liquid or liquefiable material to the base beads.

14. A method of producing a free flowing particulate detergent composition substantially as described in any of the Examples.

15. Free flowing particulate detergent compositions which have been produced by a method according to any of the preceding Claims.

16. A free flowing particulate detergent composition which comprises detergent builder beads with a liquid or liquefiable material comprising an organic detergent applied to the beads, the builder beads having a porous outer surface and a skeletal internal structure and comprising a first quantity of hydrated phosphate builder salt, a second quantity of alkali metal silicate and a third quantity of anhydrous phosphate builder salt, the weight ratio on an anhydrous basis of the first quantity to the second quantity being in the range from 1.5:1 to 5:1 and the weight ratio on an anhydrous basis of the first quantity to the third quantity being in the range from 0.3:1 to 0.7:1.

17. A detergent composition according to Claim 16 in which the builder beads

carry from 12 to 30 percent by weight of the composition of a nonionic polyethoxylated synthetic organic detergent, and in which the beads comprise by weight of the beads, from 45 to 90 percent of phosphate builder salt, from 5 to 15 percent of alkali metal silicate and from 5 to 15 percent of water.

18. A detergent composition according to Claim 17 wherein the nonionic synthetic detergent is an ethoxylated aliphatic alcohol having a carbon chain of from 8 to 22 carbon atoms and from 5 to 30 ethylene oxide units per mole.

19. A detergent composition according to any of Claims 16 to 18 wherein the phosphate builder salt comprises sodium tripolyphosphate.

20. A detergent composition according to any of Claims 16 to 19 in which the detergent is disposed within the beads and the outer surface of the beads is substantially free from the nonionic detergent.

21. A detergent composition according to any of Claims 16 to 20 having a specific gravity in the range from 0.5 to 0.7 and a flowability (as hereinbefore defined) of at least 75.

22. A detergent composition according to any of Claims 16 to 21 wherein the base beads have a particle size distribution such that at least 90 percent by weight of the beads pass through a 20 mesh screen (U.S. series) and at least 90 percent by weight are retained on a 200 mesh screen (U.S. series).

23. A detergent composition according to any of Claims 16 to 22 which includes bleach and/or enzyme applied to the beads.

24. A detergent composition according to Claim 16 comprising from 65 to 90 percent by weight of the builder beads carrying from 10 to 35 percent by weight of a nonionic polyethoxylated synthetic organic detergent, in which the beads comprise, by weight of the beads, from 45 to 90 percent of phosphate builder salt, from 5 to 15 percent of an alkali metal silicate and from 5 to 15 percent of water and have a particle size distribution such that at least 90 percent by weight of the beads pass through a 20 mesh screen (U.S. series) and are retained on a 200 mesh screen (U.S. series), and the composition has a specific gravity in the range from 0.5 to 0.7 and a flowability (as hereinbefore defined) of at least 75.

25. A detergent composition according to Claim 24 wherein the phosphate builder salt is sodium tripolyphosphate and the alkali metal silicate is sodium silicate.

26. A detergent composition according to Claim 24 or Claim 25 wherein the nonionic synthetic detergent comprises ethoxylated aliphatic alcohols having a carbon chain of from 8 to 22 carbon atoms and from 5 to 30 ethylene oxide units per mole.

27. A detergent composition according to any of Claims 24 to 26 which includes from 15 to 50% by weight of alkali metal per-salt bleach and from 0.2 to 4% by weight of protolytic enzyme added after application of the synthetic organic detergent to the base beads.

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